

MIL-53(Al) Synthesis Optimization: Investigating the Formation of an Unknown Phase

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Metal-organic frameworks (MOFs) are crystalline materials that are made up of metal-containing nodes connected by organic linkers.¹ MOFs have properties such as permanent porosity, stable framework, and large surface area, all of which make this material useful for applications such as gas storage and separation, catalysis, biomedicine, and many more.² This project focused on MIL-53(Al), an aluminum-containing MOF that is known as a “breathing” MOF because of its flexible framework that transitions between different structures (phases) depending on ambient temperature, pressure, and/or the presence of attached molecules within the pores of the MOF.^{3,4}

Previous work in the Ortol-Bloch lab has observed the formation of a formerly unknown phase of MIL-53(Al) during the calcination step of the synthesis, a process which involves heating the as-synthesized MOF product to high temperatures to remove any uncoordinated (unreacted) linker molecules from the pores of the MOF. In the literature, this unknown phase has only been observed as a result of a partial decomposition of the MOF under reflux or highly basic conditions.^{5,6} The aim of this project was twofold: to study what synthesis conditions lead to the formation of the unknown phase to ultimately prevent its formation in future work with the MOF while also isolating the unknown phase and characterizing it to further understand its composition and structure.

Firstly, in order to study the synthesis conditions leading to the formation of the unknown phase of MIL-53(Al), we synthesized the MOF under varying conditions such as different hydrothermal growth times, different work-up procedures, and different calcination temperatures and times. We analyzed all samples by powder X-ray diffraction (PXRD) to confirm the successful synthesis of our MOF and determine the relative abundance of the different phases of the MOF in each sample. We also analyzed our samples by scanning electron microscopy (SEM) to visualize crystal size, shape (morphology), and topology. Secondly, in order to characterize the unknown phase of the MOF, we calculated the linker weight of samples by quantitative nuclear magnetic resonance (qNMR) spectroscopy and tracked atomic-bond level changes of phase transitions by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR).

The calcination step of the synthesis of MIL-53(Al) was found to be the sole cause of the formation of the unknown phase, with the unknown phase forming at lower than standard calcination temperatures but disappearing after calcination at higher temperatures. The linker weight calculations and the FTIR data indicate the presence of uncoordinated linker molecules in samples of the unknown phase of MIL-53(Al), suggesting that the unknown phase is formed by the incomplete removal of linker molecules from the pores of the MOF. Moving forward, we will determine the exact lattice parameters of the unknown phase of MIL-53(Al) with the help of Yale’s Chemical and Biophysical Instrumentation Center, which will further aid in elucidating the cause of the formation of the unknown phase. I will also continue working with MIL-53(Al) to study the effects of different metal precursors on the final structure and morphology of the MOF crystals in order to better understand how factors such as defects and the rate of crystallization affect the formation of MIL-53(Al).

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Citations:

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